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Bismuth nanoparticles decorated on Na-montmorillonite-multiwall carbon nanotube for simultaneous determination of heavy metal ions-electrochemical methods



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ABSTRACT

This study presents the preparation and application of the electrochemical sensor based on pencil graphite electrode (PGE) coated with a mixture of multi-wall carbon nanotube (MWCNT) and nano size-sodium montmorillonite (NNaM). The electrode obtained was used in the electrochemical quantification of heavy metals. The electrochemical analysis was elaborated further by collecting Bi nanoparticles (BiNP) on the electrode surface during the deposition step of the analytes. The heavy metal cations, zinc (II), cadmium (II), lead (II) and copper (II) were qualified at the potentials of about −1.0, −0.70, −0.47 and 0.00 V, respectively and they quantified within the linear concentration ranges of 2.36–40.0; 40.0–180.0 μM, 0.32–2.0; 2.0–240.0 μM, 0.03–5.0; 5.0–80.0 μM and 0.52–10.0; 10.0–40.0 μM, respectively. The characterization of the electrode surfaces was made by energy-dispersive X-ray spectroscopy (EDS), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV). The surface morphology of the electrode was investigated by scanning electron microscopy (SEM). The electrode developed was coded by BiNP/MWCNT-NNaM/PGE. The electrochemical quantification results indicate that the electrode developed is a low-cost tool of high conductive surface area, capable of producing a high SWAS voltammetric signal; much better for electrochemical analysis than unmodified PGE. Repeatability and reproducibility for BiNP/MWCNT-NNaM/PGE electrode were found to be RSD < 9.5 % and RSD < 8.0 %, respectively. The interference effects of the cations Mn^{2+}, Al^{3+}, Ni^{2+}, Sb^{3+} Co^{2+}, Fe^{3+}, Cr^{3+}, Ca^{2+}, Mg^{2+} and Na_3PO_4 at concentrations ten-fold lower than the analytes are tolerable (<4.5 %). Detection limits as low as 0.707 μM, 0.097 μM, 0.008 μM, and 0.157 μM, were formed for Zn (II), Cd (II), Pb (II), and Cu (II), respectively. The designed sensor was applied to a tap water sample using the standard addition method, and the results are satisfactory.

1. Introduction

Nowadays, carbon nanotubes, with specific thermal, electrical, mechanical, and current-carrying capacity have drawn wide attention in the investigation of the fields of physics, chemistry, medical materials science, and engineerings such as field-effect transistors [1], environmental monitoring [2,3] and electrochemical applications [4–6].

Adding the nano-clay structures on the electrode surface as a stabilizer for nanoparticles (NPs) may improve the electrical properties of the electrode surface due to their effective intercalation, flexible adsorption capacity, ion exchange capacity, and relatively high surface area [7–9].

The use of nano-clays has been reported to contribute to determining organic and inorganic compounds by electrochemical methods. Recently, the authors developed a rapid, sensitive, and simple way for detecting several organic molecules in the presence of natural nano-clay minerals i.e, montmorillonite and sepiolite [10,11]. Combining monometallic nanoparticles on multi-wall carbon nanotube (MWCNT)-nano-sized sodium montmorillonite (NNaM) composite materials can further enhance the number of multi-electroactive sites and electrocatalytic activities of the materials [12–14]. The combined effect of BiNP and MWCNT provides rapid electron transfer along with synergistic effects due to the high electronegativity of Bi. The electrode made of this material has an enormous potential window, readily renewable surface, and low background current. Bi also has an excellent ability to form alloys with different metals [15–17]. Due to these advantages, we focused on fabricating Bi nanoparticle-supported MWCNT-NNaM nanocomposite for simultaneous electrochemical

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quantifications of heavy metals. These metals are important pollutants found in the environment, food, drinking water, and biological samples. As these metals are harmful to human health when they are above a threshold concentration, quick and simultaneous quantitative analysis is important.

Lead is one of the most common heavy metals. It is a metabolic poison and causes mental retardation [18]. Heavy metals like zinc and copper are also essential trace elements but toxic in excess amounts [19]. Cadmium is extremely toxic even in low concentrations, and due to its bioaccumulation in tissues, long-term exposure to cadmium may induce renal damage [20,21]. Therefore, it is important to analyze these toxic metals in the environment and drinking water. In this regard, various techniques have been developed to detect heavy metal ions, including inductively coupled plasma mass spectrometry (ICP-MS) [22], inductively coupled plasma atomic emission spectrometry (ICP-AES) [23], and atomic absorption spectroscopy (AAS) [24]. These techniques are highly sensitive and selective; however, they require relatively expensive instruments and demand complex operational procedures and long detection times. The alternative electrochemical methods have the advantages of being relatively low cost, highly sensitive, rapid, easy-to-operate, and applicable in the field [25].

Among electrochemical methods, anodic stripping voltammetry (ASV) is widely used for trace heavy metal analysis thanks to its ability to enrich the metals on the electrode surface and suitable in situ measurements [26–29]. The application of the modified pencil graphite electrodes (PGEs) in electrochemical analysis has attracted remarkable attention in recent years [30–32]. PGEs have several advantages: nontoxicity, low cost, low background currents, and affordability for single-use.

In this study, we developed economic and easy electrodes prepared by the electrochemical coating of BiNP on MWCNT-NNaM/modified PGE and used them for the simultaneous detection of Zn (II), Cd (II), Pb (II), and Cu (II) by using square wave anodic stripping voltammetry (SWASV). These electrodes have proved to be generally superior to bare PGE due to the coating's high conductivity and porous structure, shifting the reduction potential of hydrogen to more negative values and providing strong mass transfer enhancement effects.

To the best of our literature knowledge, the proposed BiNP/MWCNT-NNaM/PGE nanocomposite sensor was developed firstly by our research group with the current study. Bi and MWCNT are combined with NNaM nanocomposite to increase the electrochemical activity of the coating to facilitate the analysis at relatively lower concentrations. The sensor developed has been investigated to find its selectivity, repeatability, reproducibility, and performance in real sample applications. The electrochemical synthesis process of BiNP/MWCNT-NNaM/PGE nanocomposite is shown in Scheme 1.

2. Experimental

2.1. Reagents and solutions

The chemicals used were of analytical quality. The standard solutions of Zn (II), Cd (II), Pb (II), and Cu (II), in 3% HNO_3, at 1000 mg/L concentrations, were purchased from Merck, Darmstadt, Germany. Bismuth nitrate ($Bi(NO_3)_3$) was purchased from Sigma-Aldrich (USA). 1.0 mM $Bi(NO_3)_3$ stock solutions were prepared in double-distilled water by adding 2 or 3 drops of concentrated HNO_3

2.2. Nano-Na-montmorillonite mineral

A nano-Na-montmorillonite separated from Reşadiye (Tokat/Turkey) bentonite by hydrochloric acid purification was used as a clay mineral [33,34]. Using this analysis and electro-neutralization condition, the chemical formula for the separated fraction was evaluated as follows: the metal oxide contents in the sample were determined by Hitachi Z-8200 Atomic Absorption Spectrometer [33]. The result was calculated as the mass % of the metal oxides and given as SiO_2, 61.65; TiO, 0.30; Al_2O_3, 21.10; Fe_2O_3, 4.88; MgO, 1.98; CaO, 0.36; Na_2O, 2.14; K_2O, 0.34 and loss on ignition (LOI) 6.90.

$$Na_{0.265}K_{0.027}Ca_{0.025}(Al_{1.528}Ti_{0.015}Fe_{0.141}Fe^{2+}_{0.093}Mg_{0.188}) \times (Si_{3.939}Al_{0.06})O_{10}(OH)_2.nH_2O$$

This indicated that the fraction is almost Na-montmorillonite, having ideal formula in the following form [35]:

$$Na_{0.33}(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2.nH_2O$$

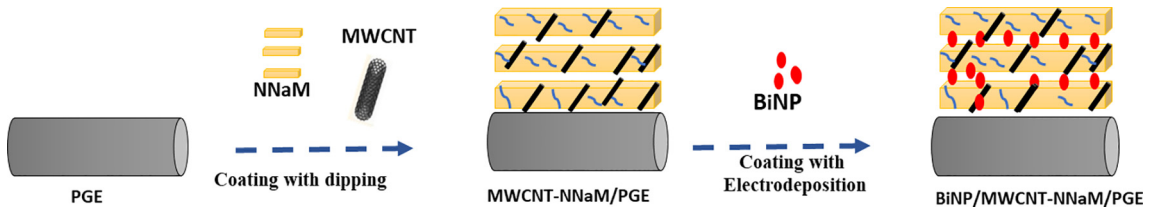
The Na-montmorillonite structure of this sample is proved by X-ray diffraction analysis [34]. The same sample's surface area and pore volume are determined from nitrogen adsorption/desorption data at 77 K to be 55 m^2/g and 7.7 × 10^{-2} cm^3/g, respectively. According to the formula, cation change capacity was measured as 1.20 mol/kg.

2.3. Apparatus

The voltammetric measurements were carried out using Palmsens*4* powered by PSTrace 5.8 software (The Netherland). Faber Castel pen tips (0.7 mm diameter and 75 mm long) were used as a working electrode and purchased from local stationery. The Electron microscopic studies were carried out using FEI Quanta 450 Field Emission Scanning Electron Microscope (FEI, The Netherlands). pH measurements were made on HANNA HI 2211 pH/ORP Meter (Smithfield, RI). Double-distilled water was delivered by the mpMINIpure dest model purification device (Turkey).

2.4. Electrochemical measurements

The electrochemical characterizations of the PGE and modified PGEs were studied by cyclic voltammetry at 50 mV/s scan rate in 1.0 M acetate buffer solution pH 4.5 with 5.0 mM $Fe[CN]_6^{3-/4-}$ in 0.1 M KCl standard solution. The known value of Zn (II), Cd (II), Pb (II), and Cu (II) stock solutions were injected into the volumetric cell with a total volume of 10.0 mL. Before all trials (CV, SWASV, and EIS) and after fixing the electrode connection, the working solutions were purged for 30 s with nitrogen gas (99.99 % pure) for oxygen removal. After this step, the electrochemical measurements were made. SWAS voltammograms were recorded at the potential windowing ranges (−1.4)–(+0.5) V using the parameters, equilibration time: 15 s; frequency: 25 Hz; potential increments: 0.005 V; amplitude: 0.025 V; 1.0 M acetate buffer solution (pH 4.5), each run being under



Scheme 1. The preparation step of BiNP/MWCNT-NNaM/PGE sensor.

optimum experimental conditions. The metals were reduced on the electrode surface in defined deposition periods and potentials during the deposition stage while stirring at a constant speed. Deposition times and potentials were optimized, and the reduced metals were stripped from the electrode by oxidation.

2.5. The preparation of modified electrodes

Scheme 1 illustrates preparing the BiNP/MWCNT-NNaM/PGE nanocomposite material. 0.1 % of MWCNT and NNaM were dispersed with chitosan (2 % (m/v) dispersed in acetic acid solution 2 % (v/v) by sonication to obtain a homogeneously distributed mixture. MWCNT and NNaM were coated by dipping the PGE into a vial containing the composite mixture and left to dry in the open air in the upside-down position. Then, the bismuth film was deposited in situ on the MWCNT-NNaM/PGE electrode by electrodeposition of the standard solution of 5.0×10^{-6} M Bi (III) in 1.0 M acetate buffer (pH 4.5) with constant stirring; while deposition of the analytes, Zn (II), Cd (II), Pb (II), and Cu (II), was occurring. The measurements were repeated five times. For comparison, electrodes representing several stages of the modification procedure were also prepared to test the benefit of each stage. In this regard, BiNP/PGE, MWCNT/PGE, and NNaM/PGE electrodes were manufactured using 0.1 % MWCNT, 0.1 % NNaM, and 5.0×10^{-6} M Bi (III) for coating.

2.6. Procedure for real sample

Tap water samples taken directly from Ankara's public water system were diluted to reach a dilution of 2:10 (tap water: acetate buffer solution) with 0.1 M acetate buffer solution (pH 4.5). Deposition times of heavy metals on the electrode surface were 180 s, with constant stirring. The SWVs were recorded in the range, (−1.4) - (+0.5) V (vs. Ag/AgCl). Finally, the concentrations of heavy metals were determined considering the dilution factor. In the recovery studies, tap water samples were spiked with known amounts of heavy metal stock solutions.

3. Results and discussion

3.1. Electrochemical properties of modified electrodes

Electrochemical impedance spectroscopy (EIS) was used to investigate the interface resistance of PGE, NNaM/PGE, MWCNT/PGE, BiNP/PGE, and BiNP/MWCNT-NNaM/PGE electrodes. To do this, a solution of 5.0 mM $Fe[CN]_6^{3-/4-}$ in 0.1 M KCl medium is used as the control analyte. The EIS spectra obtained are shown in Fig. 1a. The curves show that BiNP/MWCNT-NNaM/PGE electrode has relatively lower interfacial charge transfer resistance. This property indicates the appropriateness of the electrode concerned for electrochemical analysis. As shown in Fig. 1b, BiNP/MWCNT-NNaM/PGE has the highest peak current (549.7 μA) with a small ΔE_p of 0.04 V compared to those of BiNP/PGE (372.2 μA), NNaM/PGE (394.8 μA) and MWCNT/PGE (439.5 μA).

On the other hand, the surface area of the electrodes was found with the aid of CV scans. To do this, a 5.0 mM solution of $[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl was scanned, and the resultant CV was used for surface area calculations. The potential range (−0.5) - (+0.9) V and the scan rate, 0.05 Vs^{-1} was employed for this purpose (Fig. 1b).

The surface areas of the electrodes were calculated with the Randles-Sevcik equation. Equation (1) [36] could be used for a reversible reaction:

$$i_p = 2.69 \times 10^5 n^{3/2} A D o^{1/2} C o \upsilon^{1/2} \quad (1)$$

here, n is the number of electrons exchanged in the redox reaction; A is the electroactive surface area (cm^2); C_o is the concentration of the probe material; D_o is the coefficient of diffusion (7.6×10^{-6} $cm^2 s^{-1}$), and υ is the scan rate ($V\ s^{-1}$). The calculated electroactive surface areas for BiNP/MWCNT-NNaM/PGE, MWCNT/PGE, NNaM/PGE, BiNP/PGE and PGE are 1.733 ± 0.058 cm^2, 1.447 ± 0 0.071 cm^2, 1.298 ± 0.171 cm^2, 0.644 ± 0.003 cm^2 and 0.583 ± 0.233 cm^2, respectively. Thus, BiNP/MWCNT-NNaM/PGE electrode has the largest surface area and, therefore, has better conductivity than the other modified electrodes and PGE. This result is consistent with the conclusion of EIS studies.

We also examined the surface morphology of the PGE, BiNP/PGE, NNaM/PGE, MWCNT/PGE, and BiNP/MWCNT-NNaM/PGE electrodes by scanning electron microscopy (SEM) in Fig. S1. As shown from Fig. S1b and c, the NNaM on the PGE electrode exhibits a three-dimensional hole structure. MWCNT/PGE possesses a porous structure (Fig S1c). BiNP/MWCNT-NNaM/PGE displayed a three-dimensional porous structure, forming empty spaces well connected. Energy dispersive X-ray (EDS) spectroscopy was used to investigate the prospective elemental compositions of the coatings on the BiNP/MWCNT-NNaM/PGE composite (Fig. S1e). The relative quantities of elements are as follows: Carbon (81.51 %), oxygen (13.91%), as well as a minority of bismuth (0.40%) elements.

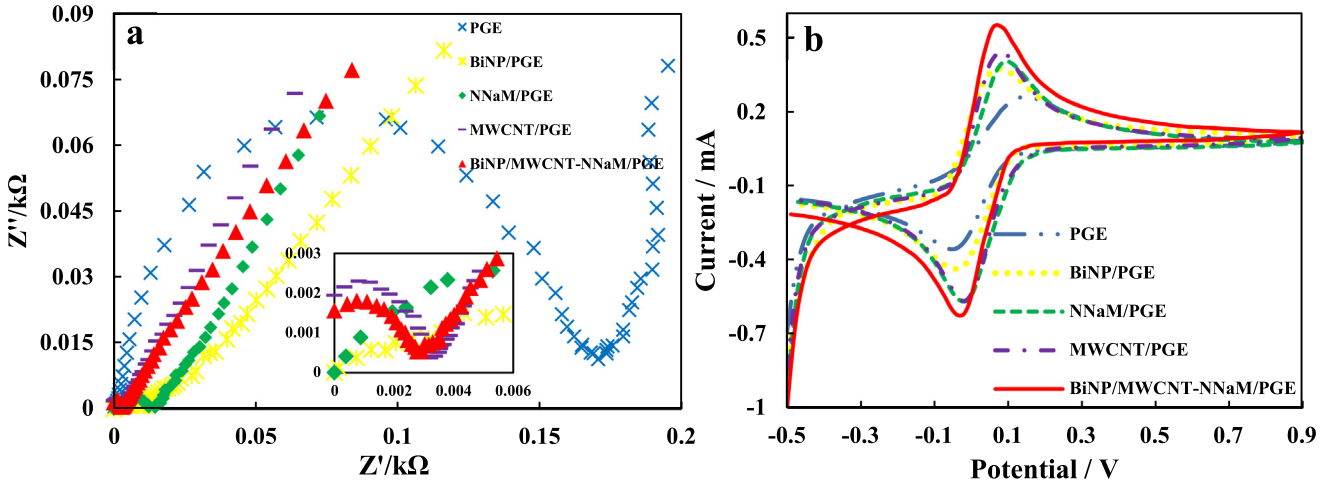


Fig. 1. a) Nyquist diagrams **b)** Cyclic voltammograms of PGE (blue), BiNP/PGE (yellow), NNaM/PGE (green), MWCNT/PGE (purple), and BiNP/MWCNT-NNaM/PGE electrodes (red) in 0.1 M KCl solution containing 5.0 mM of $[Fe(CN)_6]^{3-/4-}$ at a scan rate of 0.05 Vs^{-1}.

3.2. Simultaneous electrochemical sensing of heavy metals

The electrochemical sensing performances for Zn (II), Pb (II), Cd (II), and Cu (II), of the electrodes PGE, MWCNT/PGE, NNaM/PGE, BiNP/PGE, and BiNP/MWCNT-NNaM/PGE, were investigated by DPV measurements. Fig. 2 shows the comparison between SWAS peaks of the PGE and modified PGEs in 0.1 M acetate buffer solution (pH 4.5) containing 50.0 μM Zn (II), 5.0 μM Pb (II), 10.0 μM Cd (II) and 5.0 μM Cu (II). PGE electrode exhibited a weak peak current and broader signal for individual analytes. The electrochemical performance of NNaM-PGE and BiNP-PGE electrodes exhibited a notable change compared to PGE. In particular, BiNP/MWCNT-NNaM/PGE showed much higher peak intensities (Fig. 2). As expected, the addition of BiNP to MWCNT and NNaM significantly enhanced the performance of the electrode.

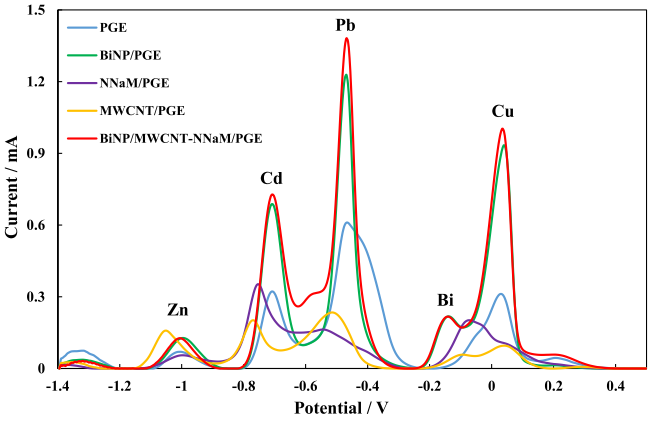


Fig. 2. SWAS voltammograms of 50.0 μM Zn (II), 5.0 μM Pb (II), 10.0 μM Cd (II) and 5.0 μM Cu (II) on PGE and different modified PGEs in 1.0 M acetate buffer solution, pH 4.5, 1.0 μM Bi(III).

To determine optimal compositions of the coating materials in the mixture used in the modification process, the percentage contents of MWCNT and NNaM were changed under controlled conditions (Fig. S2). At each trial, the mass content of one component was changed while that of the other was constant. As an example, the percentages of MWCNT was taken as 0.1, 0.2, 0.3, 0.4, and 0.5 % (w/w) while NNaM content was kept at % 0.1. The changes in the compositions of the coating materials were hardly significant, provided the contents of the two components were between 0.1% − 0.5%.

We also examined the impact of Bi (III) concentrations used in the pre-deposition stage. The trial range was 0.1 μM − 50.0 μM (Fig. S3). The results showed that the currents related to the heavy metals increased up to the concentration of 5.0 μM Bi (III) and then started to decrease with increasing Bi(III) concentration. This is especially true for Pb (II) and Cu (II). The optimal concentration of Bi(III) was chosen as 5.0 μM.

The impact of different pH values on the electrochemical response of heavy metals was investigated in the pH range 3.8–5.5. Appropriate acid/base ratios were achieved to obtain the pH desired, with 1.0 M acetate buffer. The results are shown in Fig. 3. The voltammetric signals for metals rise at pH values from 3.8 to 4.5 and gradually decrease up to pH 5.5. Probably the hydrolysis of metal ions occurred above pH 4.5 [37]. Therefore, acetate buffer solution with pH 4.5 was used for subsequent experiments.

3.3. Simultaneous voltammetric determination of the heavy metals

To obtain the best SWV signal for the simultaneous determination of the metal ions, the effect of deposition potential on peak currents was investigated in the potential range (–1.2 V) - (–2.0 V) (Fig. S4a). The peak currents for Zn (II), Pb (II), Cd (II), and Cu (II) began to rise at –1.2 V and reached their maximum value at –1.80 V. Hence; we selected –1.80 V as the optimal deposition potential for the best peak shape and the highest peak currents. Optimizing the deposition time was also achieved. For this purpose, by setting the E_{dep} to the optimum value found, the effect of deposition time on peak currents was examined within the range 0–480 s with increments of the 60 s (Fig. S4b), and the highest peak currents were achieved at a t_{dep} of 180 s.

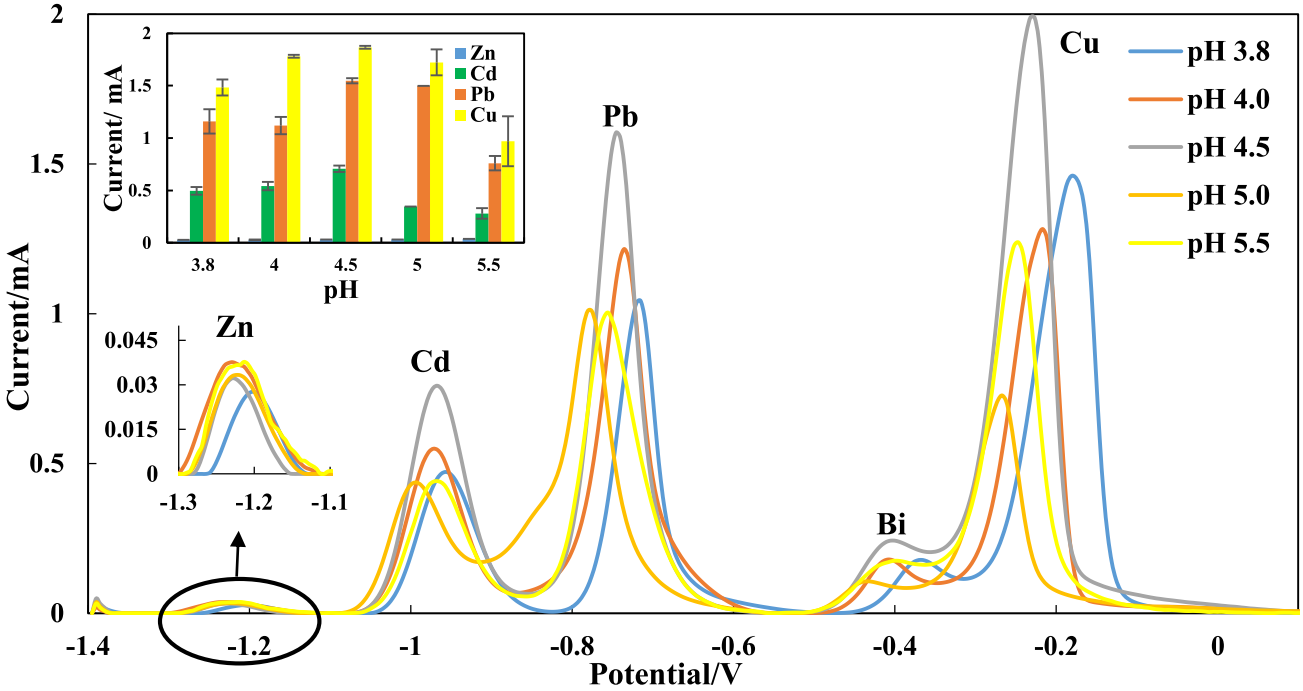


Fig. 3. SWASV voltammograms of 50.0 μM Zn (II), 5.0 μM Pb (II), 10.0 μM Cd (II) and 10.0 μM Cu (II) at different pH values in acetate buffer solution at BiNP/MWCNT-NNaM/PGE. Inset: The plot of i_p of pH on the BiNP/MWCNT-NNaM/PGE.

Table 1
Regression and validation parameters of the simultaneous calibration lines of Zn (II), Pb (II), Cd (II), and Cu (II) ions.

Regression parameters	Zn	Cd	Pb	Cu
Linear working range, μM	2.36–40.0	0.32–2.0	0.03–5.0	0.52–10.0
	40.0–180.0	2.0–240.0	5.0–80.0	10.0–40.0
Slope, mA/μM	0.003 (±0.0002)	0.1741 (±0.04)	0.2674(±0.012)	
	0.0014 (0.00042)	0.0053(±0.001)	0.0128(±0.0013)	0.1349(±0.0135)
				0.0348(±0.0024)
Limit of detection (LOD), μM	0.707	0.097	0.008	0.157
Limit of quantification (LOQ), μM	2.36	0.32	0.03	0.52
Regression coefficient (R^2)	0.9872	0.9986	0.9708	0.995
	0.9966	0.9958	0.956	0.9832
Repeatability of peak potential, RSD%[a] (intra-day)	0.06	1.96	3.53	5.71
Repeatability of peak current, RSD%[a] (intra-day)	9.31	0.30	3.83	5.73
Reproducibility of peak potential, RSD%[a]	0.35	1.16	1.14	6.35
Reproducibility of peak current, RSD%[a]	7.89	5.76	2.07	0.43

[a] RSD is the relative standard deviation of 5 replications (95% Confidence Level).

Table 2
Comparison of analytical performance at the BiNP/MWCNT-NNaM/PGE electrode with previously reported modified PGE sensors.

Electrode	Method	Analyzed metals	Working ranges, μM	LOD, μM	Sample	Lit.
Nafion-covered pencil-lead BFEs	SWASV	Zn	0.153–1.530	0.006	Tap Water	[38]
		Cd	0.088–0.889	0.003		
		Pb	0.048–0.483	0.02		
Pencil-lead graphite BiFE	SWASV	Zn	0.01–0.12	0.012		[39]
		Cd	0.01–0.12	0.003		
		Pb	0.01–0.12	0.002		
Bi/PL-Es	DPASV	Cd	0–0.89	0.178	Drinking and tap water, wastewater reference, soil sample	[40]
		Pb	0–0.48	0.009		
ERGO-PG-BiE	SWASV	Zn	0.03–0.30	0.004	Tap Water	[41]
		Cd	0.018–0.178	0.0009		
		Pb	0.009–0.096	0.0006		
NG-PG-BiE	SWASV	Zn	0.153–1.529	0.003	Tap water	[42]
		Cd	0.089–0.889	0.0008		
		Pb	0.048–0.483	0.001		
sol–gel-DIIP/PGE	DPASV	Cd	1.11×10^{-9}–5.29×10^{-8}	4.48×10^{-10}	Human hood serum, Cow's milk, Lake water samples	[43]
		Cu	1.97×10^{-9}–2.83×10^{-8}	5.35×10^{-10}		
6B PDE	ASV	Cd	0.872–3.356	0.872		[44]
		Pb	0.048–0.724	0.048		
EP-PGE	SWASV	Cd	0.089–0.356	0.0099	Standard reference water sample	[45]
		Pb	0.024–0.217	0.002		
BiFE	DPASV	Cd	0.429–2.073	0.098	Wastewater sample	[46]
		Pb	0.233–1.124	0.056		
AgNP/Bi/Nafion/PGE	ASV	Cd	0.889–8.896	0.002	Wastewater sample	[47]
		Pb	0.482–4.826	0.0014		
BiNP/Nafion modified PGE	ASV	Cd	0.088–1.334	0.065	Cow's milk samples	[48]
		Pb	0.0483–0.724	0.149		
G/Bi-PGE	SWASV	Cd	0.044–0.889	0.0011	Canadian-certified reference water, Tap water samples	[49]
		Pb	0.024–0.483	0.0014		
HF-PGE	DPV	Zn	0.014–7.312	0.004	Mineral, tap and river water samples	[50]
		Cu	0.011–7.868	0.003		
BiNP/MWCNT-NNaM/PGE	*SWASV*	*Zn*	*2.36–40.0; 40.0–180.0*	*0.707*	*Tap Water*	*Present work*
		Cd	*0.32–2.0; 2.0–240.0*	*0.097*		
		Pb	*0.03–5.0; 5.0–80.0*	*0.008*		
		Cu	*0.52–10.0; 10.0–40.0*	*0.157*		

Nafion-covered pencil-lead BFEs: Nafion-covered pencil-lead bismuth-film electrodes; Pencil lead graphite BiFEs: Bismuth film electrodes; Bi/PL-Es: Bi modified Pencil-lead electrodes; ERGO-PG-BiE: Electrochemically Reduced Graphene Oxide Pencil-Graphite in situ Plated Bismuth-film Electrode; NG-PG-BiE: Nafion-graphene nanocomposite pencil graphite bismuth-film electrode; sol–gel-DIIP/PGE: sol–gel matrix (inorganic–organic hybrid nano-material)-dual-ion imprinted polymer pencil graphite electrode; 6B PDE: 6B pencil drawn electrode; EP-PGE: Electrochemically pretreated pencil graphite electrode; BiFE: Bismuth film electrode supported on pencil graphite; AgNP/Bi/Nafion/PGE: Silver/Bismuth/Nafion Modified Pencil Graphite Electrode; BiNP/Nafion modified PGE: Pencil graphite electrode modified with bismuth nanoparticles and Nafion; G/Bi-PGE: Graphene/Bismth nanocomposite film modified pencil graphite electrode; HF-PGE: Hollow fiber-pencil graphite electrode; BiNP/MWCNT-NNaM/PGE: Pencil graphite electrode coated with a mixture of multi-wall carbon nanotube and nano size-sodium montmorillonite; SWASV: Square wave anodic stripping voltammetry; ASV: anodic stripping voltammetry; DPASV: Differential pulse anodic stripping voltammetry; DPV: Differential pulse voltammetry.

Table 3
The determination of Zn (II), Cd (II), Pb (II), and Cu (II) in tap water sample mean recovery results and the relative standard deviation.

Method	Sample	Claimed amount, μM	Found amount, μM	Average recovery, %	RSD[a], %
SWASV	Zn	20.0	20.111 ± 0.6415	99.5 ± 3.12	3.13
	Cd	20.0	20.195 ± 0.8775	99.2 ± 4.20	4.23
	Pb	20.0	20.873 ± 0.7453	95.9 ± 3.49	3.64
	Cu	20.0	20.487 ± 0.3719	97.6 ± 1.76	1.79

[a] Each value is the mean of three experiments (95% Confidence Level).

The optimized parameters were employed in the quantitative analysis of heavy metals at pH 4.5, using the SWASV method. The results found for the known concentration of the four heavy metals are shown in Fig. S5. The signals are shown proportional to concentrations within fairly broad ranges.

All the linear regression and analytical method validation parameters are listed in Table 1. Validation parameters, the limit of detection (LOD), limit of quantification (LOQ), and precision were found according to the literature [26]. The calculated LODs are as follows: 0.707 μM, 0.097 μM, 0.008 μM and 0.157 μM for Zn^{2+}, Cd^{2+}, Pb^{2+} and Cu^{2+}, respectively. RSDs for peak currents of each metal ion demonstrated good repeatability. The reproducibility of BiNP/MWCNT-NNaM/PGE was also investigated. The three groups of sensors go through the same process and are then used simultaneously to identify heavy metal ions. The similar responses of each electrode showed excellent reproducibility (RSD% < 8.0 for peak current and potential) (Table 1). These results indicate the good stability and reusability of the BiNP/MWCNT-NNaM/PGE despite the single-use nature of the PGEs.

The analytical performances were compared with the PGE electrodes reported binary and ternary analysis of metals in the literature and are summarized in Table 2. These findings show that the developed sensor exhibits an electrocatalytic superiority activity, good linearity range, and comparable detection.

3.4. Interference studies

The selective determination of heavy metals was investigated in 0.1 M acetate buffer using SWASV. Fig S6 shows SWASV response to heavy metals over possible interference metals (Mn^{2+}, Al^{3+}, Ni^{2+}, Sb^{3+} Co^{2+}, Fe^{3+}, Cr^{3+}, Ca^{2+}, Mg^{2+} and Na_3PO_4). The response currents were compared with peak currents in the absence of interfering agents (Fig. S6). Considering the low concentration of heavy metals, (in the order of μg/L) in water [51], all interfering agents were kept at a 10:1 ratio (analyte: interfering metal). The result shows that the ions tested have no significant interference (all below 4.5 %). Then, the practical application of the modified sensor was investigated in the real sample.

3.5. Analysis of real sample and recovery

The main applications of voltammetric heavy metal analysis are performed in food, environment and, various water samples such as surface water, tap water, wastewater, etc. In our case, to demonstrate the analytical applicability of the proposed sensor, tap water was directly analyzed using BiNP/MWCNT-NNaM/PGE electrode. To minimize the effect of interferences, the standard addition method was used. Recovery studies were carried out with the standard addition method in which known amounts of the standard solutions of the analyte are added to the tap water sample. The statistical results and percentage recovery studies are presented in Table 3. A good agreement was found between the added and the obtained analyte concentrations. The recovery values were 99.5% and 95.9% (Table 3). These results demonstrate that the developed method's precision and accuracy are acceptable.

4. Conclusion

Monometallic bismuth film obtained by in situ electrochemical coating on the surface of PGE electrodes co-modified with MWCNT and NNaM was prepared with a straightforward approach. Compared to electrodes BiNP/PGE, MWCNT/PGE, and NNaM/PGE, the BiNP/MWCNT-NNaM/PGE exhibit a notable synergistic increase in the SWASV signals of heavy metals. The sensor shows a wide linear range, a reasonable limit of detection, and an acceptable limit of quantification. On the other hand, the structural and electrochemical characterizations of the nanocomposite BiNP/MWCNT-NNaM/PGE indicate a large surface area and low interfacial resistance. The developed method was applied for the detection of Zn (II), Cd (II), Pb (II), and Cu (II) in tap water. The results show that the electrode developed may open up a new way to analyze toxic trace elements.

CRediT authorship contribution statement

Ceren Yıldız: Investigation, Data curation. **Dilek Eskiköy Bayraktepe:** Resources, Investigation, Data curation, Writing – review & editing. **Zehra Yazan:** Supervision, Conceptualization, Methodology, Validation, Funding acquisition, Project administration, Writing – review & editing. **Müşerref Önal:** Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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